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54 Process for the preparation of acetal polymer or copolymer.

57 An acetal polymer and copolymer are prepared by polymerizing formaldehyde or its cyclic oligomer as a principal monomer or copolymerizing said principal monomer with a comonomer copolymerizable therewith, characterized by using an isopoly acid or an acid salt thereof as a polymerization catalyst.

EP 0 347 119 A2

PROCESS FOR THE PREPARATION OF ACETAL POLYMER OR COPOLYMER

The present invention relates to a process for the preparation of an acetal polymer or copolymer.

Particularly, it relates to a novel process for the preparation of an acetal polymer or copolymer which comprises polymerizing formaldehyde or a cyclic oligomer thereof as a principal monomer, characterized by using an isopoly acid or an acid salt thereof as a catalyst.

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[Prior Art]

Oxyalkylene polymers represented by an oxymethylene polymer comprising repeating units of $-CH_2O-$ have been known for long and the processes for the preparation thereof according to the prior art can be broadly classified into two types. One of the them comprises a process characterized by polymerizing anhydrous formaldehyde as a principal monomer, while the other thereof comprises a process characterized by polymerizing, as a principal monomer, a cyclic acetal such as trioxane which is a cyclic trimer of formaldehyde.

With respect to the former process, it has been proposed to polymerize or copolymerize substantially anhydrous formaldehyde in the presence of an anionically or cationically active catalyst, while with respect to the latter process, it has been proposed to polymerize or copolymerize a cyclic acetal such as trioxane in the presence of a cationically active catalyst. The catalyst which has been proposed for the above processes includes Lewis acids, particularly, halides of boron, tin, titanium, phosphorus, arsenic or antimony, such as boron trifluoride, tin tetrachloride, titanium tetrachloride, phosphorous pentachloride, phosphorus pentafluoride, arsenic pentafluoride and antimony pentafluoride and complexes and salts thereof; proton acids such as perchloric acid; esters of proton acids, particularly, esters of perchloric acid with lower aliphatic alcohols, such as t-butyl perchlorate; anhydrides of proton acids, particularly, mixed anhydrides of perchloric acid with lower aliphatic carboxylic acids such as acetyl perchlorate; trimethyloxonium hexafluorophosphate, triphenylmethyl hexafluoroarsenate, acetyl tetrafluoroborate, acetyl hexafluorophosphate and acetyl hexafluoroarsenate. Among them, boron fluoride and coordination compounds thereof with organic compounds such as ethers are the most general catalysts for the polymerization or copolymerization of a cyclic oligomer of formaldehyde such as trioxane and are industrially used in a wide field. However, the polymer prepared by using any of the above catalysts has a limited degree of polymerization. Therefore, it is very difficult to prepare a polymer having a degree of polymerization exceeding a certain limit according to the prior art.

Further, when a cyclic ether or cyclic formal having two or more adjacent carbon atoms is copolymerized with a principal monomer as described above by the process according to the prior art for the purpose of introducing a stable unit, the copolymer obtained just after the copolymerization has generally a thermally unstable moiety on its terminal, so that the copolymer must be stabilized by eliminating the unstable moiety prior to its practical use, thus necessitating complicated post-treatment consuming much energy uneconomically. If the content of an unstable moiety in a crude acetal copolymer directly obtained by copolymerization is reduced, the final product will be more stable and the post-treatment will be advantageously simplified. Thus, it has been expected to establish a copolymerization process for preparing an acetal copolymer containing a reduced amount of an unstable moiety formed during the polymerization.

[Summary of the Invention]

The reason for the above problems with respect to the limitation in the degree of polymerization of an acetal (co)polymer and the presence of a considerable amount of an unstable terminal moiety in an acetal copolymer is presumably because a polymerization catalyst as described above not only accelerates the polymerization but also affects the decomposition and depolymerization. That is, the molecular weight, thermal stability, processability in molding and color of an acetal (co)polymer vary depending upon the kind of the catalyst used. From this point of view, the inventors of the present invention have made eager studies upon polymerization catalysts and have found a polymerization catalyst which can overcome the above problems. The present invention has been accomplished on the basis of this finding.

Namely, the present invention relates to a process for the preparation of an acetal polymer or copolymer which comprises polymerizing formaldehyde or a cyclic oligomer thereof alone or copolymerizing formaldehyde or a cyclic oligomer thereof as a principal monomer with a comonomer copolymerizable

therewith, characterized by using an isopoly acid or an acid salt thereof as a polymerization catalyst.

According to the present invention characterized by using, as a polymerization catalyst, an isopoly acid or an acid salt thereof, the use of which as a polymerization catalyst has not been known as yet and the application of which to the preparation of an oxymethylene polymer has not been proposed as yet, the homopolymerization of formaldehyde or a cyclic oligomer thereof such as trioxane and the copolymerization of formaldehyde or a cyclic oligomer thereof as a principal monomer with a comonomer copolymerizable therewith can be carried out more easily than those according to the prior art and the degree of polymerization of the obtained polymer is higher than that of the polymer prepared by using the catalyst of the prior art, even if the amount of the catalyst is very small. Further, when the copolymerization is carried out according to the present invention, the obtained acetal copolymer is reduced in the content of an unstable terminal moiety. Therefore, the acetal (co)polymer prepared according to the present invention can be applied to a specific use to which the one prepared according to the prior art could not be applied. Thus, the present invention provides an acetal (co)polymer which is applicable to a widened range of use.

The isopoly acid to be characteristically used in the present invention as a polymerization catalyst is also called "homopoly acid" and refers to a high-molecular weight inorganic oxy acid formed by the condensation of an inorganic oxy acid containing only one kind of metal. A salt of an isopoly acid is represented by the general formula:

$m M_1^I O \cdot n M_2^{IV} \cdot x H_2O$ or $m M_1^I O \cdot n M^{IV} O_3 \cdot x H_2O$, wherein M^I is mainly an alkali metal; M^{IV} is vanadium, niobium or tantalum which is a Group V metal of the periodic table and M^{VI} is chromium, molybdenum, tungsten or uranium which is a Group VI metal thereof. A free isopoly acid can be prepared from a salt thereof as described above by, for example, treating a solution of the salt with an ion exchange resin or by adding a mineral acid to a concentrated solution of the salt and extracting the generated free acid with ether from the resulting mixture. Further, acid salts of an isopoly acid which are obtained by replacing a part or the whole of the protons of the isopoly acid with various metals may be also used in the present invention as a catalyst.

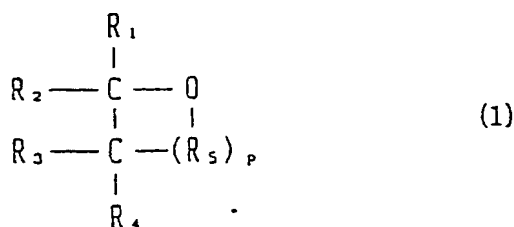
Particular examples of the isopoly acid to be used in the present invention include isopolytungstic acids such as paratungstic and metatungstic acids; isopolymolybdic acids such as paramolybdic and metamolybdic acids and isopolyvanadic acids, among which isopolytungstic acids are preferred.

The amount of the isopoly acid or acid salt thereof to be used as a polymerization catalyst varies depending upon the kind of the catalyst and the polymerization can be also controlled by changing the amount thereof. The amount is generally 0.1 to 5000 ppm, preferably 0.2 to 50 ppm, based on the total amount of the monomers to be polymerized. When an isopoly acid, having a very high activity such as paratungstic acid is used, only an amount of 0.2 to 10 ppm thereof is sufficiently effective. The fact that the polymerization or copolymerization can be carried out by using a catalyst even in such a small amount is effective in depressing the cleavage of the main chain of the polymer or depolymerization thereof caused by a catalyst and is economically advantageous.

According to the present invention, it is preferable from the standpoint of the homogeneity of the reaction to use an isopoly acid in a state dissolved in an inert solvent which does not exert any adverse effects on the polymerization of formaldehyde or a cyclic oligomer thereof and the solvent includes ethers in which an isopoly acid is soluble, particularly n-butyl ether.

The principal monomer according to the present invention is anhydrous formaldehyde or a cyclic oligomer thereof and the oligomer includes trioxane and tetraoxane which are a cyclic trimer of formaldehyde and a cyclic tetramer thereof, respectively. Particularly, trioxane is the most representative monomer in both the polymerization and the copolymerization.

Although the process of the present invention is effective in the homopolymerization of formaldehyde or a cyclic oligomer thereof, it is particularly effective in the copolymerization of formaldehyde or a cyclic oligomer thereof as a principal monomer with a comonomer. Further, the process of the present invention is effective not only in the copolymerization of formaldehyde or a cyclic oligomer thereof, such as trioxane, with one comonomer but also in the copolymerization thereof with two or more comonomers. The comonomer includes monomers which give a copolymer having a branched or crosslinked structure. Representative examples of the comonomer to be used in the present invention includes compounds represented by the general formula:



wherein R_1 , R_2 , R_3 and R_4 may be the same or different from each other and each stand for a hydrogen atom, an alkyl group or a halogen-substituted alkyl group; R_5 stands for a methylene or oxymethylene group, an alkyl- or haloalkyl-substituted methylene or oxymethylene group (in these cases, p is an integer of 0 to 3) or a divalent group of $\{CH_2\}_q OCH_2-$ or $\{O-CH_2-CH_2\}_q OCH_2-$ (in these cases, p is 1 and q is an integer of 1 to 4). The alkyl groups each have 1 to 5 carbon atoms and 1 to 3 hydrogen atoms thereof may be replaced with halogen atoms, particularly chloride atoms.

Particular examples of the compound include epichlorohydrin, ethylene oxide, 1,3-dioxolane, diethylene glycol formal, 1,4-butanediol formal, 1,3-dioxane and propylene oxide. Further, the comonomer includes cyclic esters such as β -propiolactone and vinyl compounds such as styrene and acrylonitrile. Examples of the comonomer which can give a copolymer having a branched or linear structure include alkyl mono (or di)glycidyl ethers (or formals) such as methyl glycidyl formal, ethyl glycidyl formal, propyl glycidyl formal, butyl glycidyl formal, ethylene glycol diglycidyl ether, triethylene glycol diglycidyl ether and bis(1,2,6-hexanetriol) triformal. Particularly, the advantageous effects of the catalyst according to the present invention are exhibited more effectively in the copolymerization of trioxane as a principal monomer with a cyclic ether or formal such as ethylene oxide, dioxolane or 1,4-butanediol formal as a comonomer.

In the polymerization process of the present invention, a conventional chain transfer agent such as a low-molecular weight linear acetal may be simultaneously used for the purpose of controlling the degree of polymerization depending upon the object.

The polymerization process of the present invention may be carried out in a similar manner to the one for the polymerization of formaldehyde or trioxane according to the prior art with equipment similar to the one used in the polymerization thereof according to the prior art. That is, the process of the present invention may be carried out by either a batchwise method or a continuous one and according to any of gas phase polymerization, solution polymerization, melt polymerization, melt bulk polymerization and solid phase polymerization. Particularly, a process characterized by using a liquid monomer and obtaining the objective polymer as a solid power or lump with the progress of the polymerization is generally employed. If necessary, an inert liquid medium may be used together in this process.

The polymerization equipment to be used for carrying out the process of the present invention by a batchwise method includes ordinary reaction vessels fitted with a stirrer, while the one for carrying out the process by a continuous method includes cokneaders, twin-screw continuous extruders, continuous mixers of two-shaft paddle type and other which have been proposed for the continuous polymerization of trioxane or the like. Further, combinations of two or more of these equipments may be used.

The polymerization temperature is not particularly limited and varies depending upon the method of polymerization or the kind of the monomer used. When trioxane is polymerized as a principal monomer according to an ordinary bulk polymerization method, the polymerization temperature is 64 to 120°C. Further, although the polymerization time varies depending upon the amount of the catalyst used and is not particularly limited, it is generally selected within the range of 0.5 to 100 minutes. The polymer taken out of the outlet of the polymerization equipment after the lapse of a predetermined time is generally in a state of a lump or a powder. The polymer is partially or completely rid of unreacted monomers and transferred to the following step. It is preferred that a catalyst deactivator or a solution thereof be added to the reaction mixture after the completion of the polymerization to neutralize and deactivate the catalyst present therein. Examples of the deactivator include ammonia, amines such as triethylamine and tri-*n*-butylamine, hydroxides of alkali metals or alkaline earth metals and the like. When the formed polymer is in a state of a big lump, it is a matter of course that it is preferable to pulverize the lump prior to the deactivation treatment.

The polymer thus treated is generally treated for stabilization. When the polymer is a homopolymer, the stabilization thereof is attained by converting the terminal group into an ester, ether or urethane group to thereby carry out the blocking thereof, while when the polymer is a copolymer, the copolymer is heat-melted or heated in a liquid medium in which the copolymer may be either soluble or insoluble to thereby decompose and eliminate an unstable moiety selectively, thus attaining stabilization. Particularly, the copolymer prepared according to the present invention contains a reduced amount of an unstable moiety as

compared with the one prepared according to the prior art, so that the stabilization thereof can be remarkably simplified and the obtained final product is highly stable.

As illustrated in the above description and below Examples, the process for the preparation of an acetal polymer or copolymer according to the present invention gives a polymer having an enhanced molecular weight in an enhanced polymerization yield on a very low catalyst level as compared with the process of the prior art. Further, when an acetal copolymer is prepared according to the present invention, the copolymer contains a reduced amount of an unstable moiety, so that it can give a final product excellent in stability after post-treatment and that the post-treatment itself can be economically simplified.

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[Example]

The examples given below illustrate the present invention, but it is to be understood that the invention is not limited to them. The terminology and methods of measurement used in the Examples and Comparative

15 Examples are as follows:

% or ppm : all by weight

Polymerization yield : percentage by weight of the obtained polymer based on the whole monomers used.

Solution viscosity [reduced viscosity]:

20 A polymer was dissolved in 50 g of p-chlorophenol containing 2 % of α -pinene. The obtained solution was examined for solution viscosity at 60 °C (evaluated as a characteristic value corresponding to the molecular weight)

Melt index (MI) :

25 The melt index (g/10 min) determined at 190 °C is shown. It was evaluated as a characteristic value corresponding to the molecular weight. That is, the lower the MI, the higher the molecular weight. (prior to the measurement of the melt index, a small amount of a certain stabilizer was added to the polymer to thereby inhibit the decomposition thereof during the measurement).

Degree of alkali decomposition (content of unstable moiety) :

30 1 g of a copolymer was added to 100 ml of 50 % aqueous methanol containing 0.5 % of ammonium hydroxide. The obtained mixture was heated at 180 °C for 45 minutes in a sealed vessel to determine the amount of the formaldehyde formed by the decomposition and dissolved in the liquid medium. The content is shown by percentage based on the copolymer.

Loss in weight on heating:

35 5 g of a copolymer was pulverized and mixed with a powdery stabilizer mixture comprising 2,2'-methylenebis(4-methyl-6-*t*-butyl-phenol) (0.5 % by weight) and dicyandiamide (0.1 %). The obtained mixture was heated at 220 °C in the air for 45 minutes to determine the weight loss.

Example 1 and Comparative example 1

40 200 ml of a solution of 0.04 g of paratungstic acid in *n*-butyl ether was fed into a 500-ml separable flask fitted with a gas inlet tube and a stirrer. Formaldehyde gas prepared by the thermal decomposition of α -polyoxymethylene at 180 °C and passed through a trap of -190 °C to carry out the purification was introduced into the flask through the gas inlet tube at a rate of 0.35 g/min, while introducing helium gas thereinto at a rate of 50ml/min as a carrier. A powdery polymer was immediately formed. After 120 minutes 45 from the initiation of the introduction of formaldehyde, the formed powdery polymer was taken out, washed with acetone and dried to determine the polymerization yield and the reduced viscosity. The results are shown in Table 1.

The same procedure as the one described in Example 1 was repeated except that 0.13 g of boron trifluoride dibutyl etherate was used instead of the paratungstic acid. The results are shown in Table 1.

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Table 1

	Polymerization catalyst	Catalyst concentration g/l	Polymerization yield (%)	Reduced viscosity (dl/g)
Ex. 1	paratungstic acid	0.20	77	1.68
Comp. Ex. 1	boron trifluoride dibutyl etherate	0.65	73	1.28

Examples 2 and 3 and Comparative Example 2

200 g of trioxane was placed in a hermetically sealed autoclave fitted with a jacket for circulating a heating medium and an agitating blade, followed by stirring. The bulk temperature was kept at about 70 °C by circulating hot water of 70 °C through the jacket. A solution of a catalyst given in Table 2 (an isopoly acid was used as a solution in n-butyl ether, while boron trifluoride dibutyl etherate was used as a solution in cyclohexane) was added so as to give a catalyst concentration (based on the monomer) given in Table 2, thereby initiating the polymerization. After 3 minutes, 300 g of water containing 0.1 % of tributylamine was added to the autoclave to stop the reaction. The contents were taken out, pulverized into 200 mesh or smaller, washed with acetone and dried to determine the polymerization yield and the reduced viscosity. The results are shown in Table 2.

Table 2

	Polymerization catalyst	Catalyst * concentration (ppm)	Polymerization yield (%)	Reduced viscosity (dl/g)
Ex. 2	paratungstic acid	2	72	2.10
Ex. 3	paratungstic acid	4	68	2.05
Comp. Ex. 2	boron trifluoride dibutyl etherate	40 (in terms of BF ₃)	63	1.75

* based on the total amount of the monomer

As shown in Tables 1 and 2, when an isopoly acid was used as a polymerization catalyst, an enhanced polymerization yield was attained on a very low catalyst level and the obtained polymer had an enhanced molecular weight, as compared with the case of using the boron trifluoride dibutyl etherate catalyst according to the prior art.

Examples 4 to 7 and Comparative Example 3

The same polymerization and post-treatment as those described in Example 2 were repeated except that trioxane containing 3.3 % of 1,3-dioxolane was used instead of the trioxane monomer and that an isopoly acid (Examples) given in Table 3 or boron trifluoride dibutyl etherate (Comparative Example) was added as a catalyst so as to give a concentration given in Table 3. The characteristics of the obtained polymers are shown in Table 3. It has been confirmed that the use of an isopoly acid as a polymerization catalyst even on a very low level gives a high polymerization yield and that the polymer prepared by using the catalyst has a high molecular weight and excellent resistance to alkali and heat.

Example 8 and Comparative Example 4

The same polymerization and post-treatment as those described in Example 4 were repeated except that 1,4-butanediol formal was used as a comonomer instead of the 1,3-dioxolane. Separately, as Compara-

tive Example, the same procedure as the one described in Example 8 was repeated except that boron trifluoride dibutyl etherate was used as a catalyst. The results are shown in Table 3. The results were nearly equal to those obtained in the abovementioned Examples and Comparative Example.

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Table 3

	Polymerization catalyst	Catalyst * concentration (ppm)	Comonomer	Polymerization yield (%)	MI (g/10 min)	Degree of alkali decomposition	Loss in weight on heating (%)
Example 4	paratungstic acid	2	1,3-dioxolane	71	5.6	4.6	4.7
" 5	"	4	"	78	5.8	4.7	4.8
" 6	metatungstic acid	4	"	65	6.0	4.8	4.9
" 7	"	8	"	68	6.1	4.9	4.9
Comparative Example 3	boron trifluoride dibutyl etherate	40 (in terms of BF ₃)	"	62	8.3	7.1	7.2
Example 8	paratungstic acid	2	1,4-butanediol formal	70	5.9	4.7	4.9
Comparative Example 4	boron trifluoride dibutyl etherate	40 (in terms of BF ₃)	"	60	8.5	7.4	7.6

* based on the trioxane

Examples 9 and 10 and Comparative Example 5

5 A continuous mixing reactor which comprises a barrel having a section comprising two circles each having an inner diameter of 80 mm and partially overlapping each other and an effective length of 1.3 m and fitted with a jacket for passing a heating medium on the outer surface thereof and two rotating shafts fitted with many paddles was used. Hot water of 80 °C was passed through the jacket and the shafts were rotated in the directions different from each other at a rate of 100 rpm. Trioxane containing 3.3 % of 1,3-
10 dioxolane was continuously fed into one end of the reactor at a rate of 10 kg/hr, while continuously feeding a catalyst given in Table 4 so as to give a concentration given in Table 4. Thus, the copolymerization was carried out. The reaction mixture discharged from the other end of the reactor was immediately thrown into water containing 0.1 % of triethylamine to deactivate the polymerization catalyst. The polymer was dried. The characteristics thereof are shown in Table 4. According to such a continuous polymerization method as
15 well as a batchwise method using an autoclave or the like, a copolymer which has an enhanced degree of polymerization and is superior in resistance to alkali and heat was obtained in an enhanced polymerization yield by using an isopoly acid as a catalyst even on a very low level, as compared with the case of using the boron trifluoride dibutyl etherate catalyst of the prior art.

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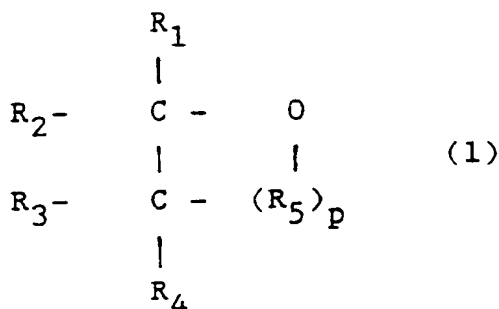
Table 4

	Polymerization catalyst	Catalyst * concentration (ppm)	Comonomer	Polymerization yield (%)	MI (g/10 min)	Degree of alkali decomposition (%)	Loss in weight on heating (%)
Example 9	paratungstic acid	2	1,3-dioxolane	74	4.7	2.0	2.2
Example 10	metatungstic acid	4	"	73	4.8	2.1	2.3
Comparative Example 5	boron trifluoride butyl etherate	40 (in terms of BF ₃)	"	66	7.0	3.9	4.1

* based on the trioxane

Claims

1. A process for the preparation of an acetal polymer or copolymer which comprises polymerizing formaldehyde or a cyclic oligomer thereof as a principal monomer or copolymerizing said principal monomer with a comonomer copolymerisable therewith, characterized by using an isopoly acid (as hereinbefore defined) or an acid salt thereof as a polymerization catalyst.
2. A process for the preparation of an acetal polymer or copolymer as set forth in claim 1, wherein said isopoly acid is an isopoly acid of tungsten.
3. A process for the preparation of an acetal polymer or copolymer as set forth in claim 2, wherein said isopoly acid is selected from one or more paratungstic acids and metatungstic acids.
4. A process for the preparation of an acetal polymer or copolymer as set forth in any preceding claim, wherein said isopoly acid is used in an amount of 0.1 to 5000 ppm (by weight) based on the total amount of the monomers used.
5. A process for the preparation of an acetal polymer or copolymer as set forth in claim 4, wherein said isopoly acid is used in an amount of 0.2 to 50 ppm (by weight) based on the total amount of the monomers used.
6. A process for the preparation of an acetal polymer or copolymer as set forth in any preceding claim, wherein said isopoly acid is dissolved in an inert solvent which does not adversely affect the polymerization.
7. A process for the preparation of an acetal polymer or copolymer as set forth in any preceding claim, wherein said comonomer is a compound represented by the general formula:



wherein R_1 , R_2 , R_3 and R_4 may be the same or different from each other and each stand for a hydrogen atom, an alkyl group or a halogen-substituted alkyl group; R_5 stands for a methylene or oxymethylene group, an alkyl or haloalkyl-substituted methylene or oxymethylene group (in which cases, p is an integer of 0 to 3) or a divalent group of $-(CH_2)_q-OCH_2$ or $-(O-CH_2-CH_2)_q-OCH_2$ (in which cases p is 1 and q is an integer of 1 to 4).

8. A process for the preparation of an acetal polymer or copolymer as set forth in any preceding claim, wherein said principal monomer is trioxane.
9. A process for the preparation of an acetal polymer or copolymer as set forth in claim 8, wherein said comonomer is a cyclic ether or a cyclic formal.
10. A process for the preparation of an acetal polymer or copolymer as set forth in any preceding claim, wherein a catalyst deactivator or a solution thereof is added to the reaction mixture after the completion of the polymerization to neutralize and deactivate the catalyst.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	EP-A-0 129 369 (POLYPLASTICS CO. LTD.) * page 6, line 12 - page 7, line 9 * ---	1	C 08 G 2/06 C 08 G 2/10 C 08 G 2/08 C 08 G 2/18
A	PATENT ABSTRACTS OF JAPAN vol. 9, no. 108 (C-280)(1831), 11 May 1985; & JP-A-601179 (MITSUI SEKIYU KAGAKU KOGYO K.K.) 07.01.1985 * abstract * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 08 G B 01 J
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 24-09-1990	Examiner VOIGTLAENDER R O J
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